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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification 5 : B01J 23/89, 23/64 C07D 307/08</p>		<p>A1</p>	<p>(11) International Publication Number: WO 92/02298 (43) International Publication Date: 20 February 1992 (20.02.92)</p>
<p>(21) International Application Number: PCT/US91/05165 (22) International Filing Date: 26 July 1991 (26.07.91)</p>		<p>(74) Agents: YUN, Caroline, J. et al.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).</p>	
<p>(30) Priority data: 558,991 27 July 1990 (27.07.90) US 734,844 24 July 1991 (24.07.91) US</p>		<p>(81) Designated States: AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CA, CF (OAPI patent), CG (OAPI patent), CH (European patent), CI (OAPI patent), CM (OAPI patent), CS, DE (European patent), DK (European patent), ES (European patent), FI, FR (European patent), GA (OAPI patent), GB (European patent), GN (OAPI patent), GR (European patent), HU, IT (European patent), JP, KP, KR, LK, LU (European patent), MC, MG, ML (OAPI patent), MN, MR (OAPI patent), MW, NL (European patent), NO, PL, RO, SD, SE (European patent), SN (OAPI patent), SU, TD (OAPI patent), TG (OAPI patent).</p>	
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<p>(54) Title: HYDROGENATION CATALYST AND METHOD FOR PREPARING TETRAHYDROFURAN</p>			
<p>(57) Abstract</p> <p>Hydrogenation in a back-mixed reactor or plug flow reactor of a hydrogenatable precursor such as maleic acid to tetrahydrofuran in the presence of a tri- or polymetallic catalytic composite consisting essentially of a combination of a catalytically effective amount of palladium, rhenium and one or more metals selected from rhodium, cobalt, platinum, ruthenium, iron, thulium, cerium, yttrium, neodymium, aluminum, praesodymium, holmium, copper, samarium, europium, hafnium, manganese, vanadium, chromium, gold, terbium, lutetium, nickel, scandium and niobium deposited on a support such as an activated, porous carbon carrier; and the continuous hydrogenation of a hydrogenatable precursor to tetrahydrofuran with hydrogen in a back mixed reactor in the presence of a suitable hydrogenation catalyst with continuous tetrahydrofuran removal while maintaining the concentration of acid within a predetermined range.</p>			

+ DESIGNATIONS OF "SU"

It is not yet known for which States of the former Soviet Union any designation of the Soviet Union has effect.

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TITLE

HYDROGENATION CATALYST AND METHOD
FOR PREPARING TETRAHYDROFURAN

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CROSS-REFERENCE TO EARLIER FILED APPLICATION

This application is a continuation-in-part of application Serial No. 07/558,991, filed July 27, 1990.

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BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

The present invention relates to the hydrogenation of hydrogenatable precursors to tetrahydrofuran in a back-mixed or a plug flow reactor in the presence of a novel tri- or polymetallic catalytic composite consisting essentially of a combination of: (1) a catalytically effective amount of palladium (Pd); (2) a catalytically effective amount of rhenium (Re); and, (3) a catalytically effective amount of one or more metals selected from rhodium (Rh), cobalt (Co), platinum (Pt), ruthenium (Ru), iron (Fe), thulium (Tm), cerium (Ce), yttrium (Y), neodymium (Nd), aluminum (Al), praesodymium (Pr) holmium (Ho), copper (Cu), samarium (Sm), europium (Eu), hafnium (Hf), manganese (Mn), vanadium (V), chromium (Cr), gold (Au), terbium (Tb), lutetium (Lu), nickel (Ni), scandium (Sc) and niobium (Nb) deposited on a support, i.e., carrier.

In another aspect, the present invention relates to an efficient aqueous process for the manufacture of high purity tetrahydrofuran comprising continuous hydrogenation of a hydrogenatable tetrahydrofuran precursor in the presence of a suitable hydrogenation catalyst in a back mixed

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reactor and maintaining the concentration of the acid in the reaction mixture within a predetermined range.

DESCRIPTION OF RELATED ART

5 Numerous catalysts are disclosed in the art as being useful for preparing tetrahydrofuran ("THF") and 1,4-butanediol ("BDO") by the hydrogenation of suitable THF precursors such as maleic acid, maleic anhydride, fumaric acid, succinic acid, malic acid, 10 dimethyl succinate and gamma-butyrolactone. Many of these catalysts incorporate the metals palladium and rhenium on a suitable support. For example, U.S. Patent 4,609,636 describes the use of a catalyst composite comprising palladium and rhenium on a carbon 15 support for making THF, BDO or mixtures thereof from a variety of hydrogenatable precursors. U.S. Patent 4,973,717 discloses the batchwise or continuous production of an alcohol and/or ether from a carboxylic acid ester using, for example, a palladium 20 based catalyst and further discloses the important effect of a metal capable alloying with palladium. The use of these alloyed catalysts for the direct, selective production of THF/BDO from precursors containing one or more carboxylic acid groups is not 25 disclosed in U.S. Patent 4,973,717.

30 Methods are known in the art for the selective production of THF by the catalytic reduction of hydrogenatable precursors. For example, U.S. Patent 4,609,636 teaches that the relative ratio of THF to BDO can be increased by increasing one or more variables selected from operating temperature, contact time, and hydrogen spacetime. It is also known from numerous references, such as U.S. Patent 3,726,905, 35 that the dehydration of BDO to give THF is catalyzed by acid and that increasing the acid concentration

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results in an increase in the relative ratio of THF to BDO. However, it is also known that rhenium containing hydrogenation catalysts are inhibited by acids in the presence of water. Bulletin of The Japan 5 Petroleum Institute, Volume 12, pages 89 to 96 (1970) describes a "kinetic study of the hydrogenation of maleic anhydride and intermediates using nickel-rhenium catalyst on kieselguhr" and reports that "water and succinic acid may be considered as the 10 chief inhibitor components" of the step involving the reduction of the intermediate succinic anhydride to gamma-butyrolactone. The authors conclude that "in order to make the THF production rate greater, it is necessary to decrease the concentration of succinic 15 acid as much as possible".

Other known catalysts and processes for the production of THF from hydrogenatable precursors are cited in the above mentioned teachings, and are useful for their intended purposes, however, all are subject 20 to improvement.

One important area subject to improvement is catalyst performance, i.e., selectivity, space time yield and activity. Selectivity is defined herein to refer to a measure of the percentage of the exit 25 stream composed of THF/BDO/gammabutyrolactone ("GBL") in a plug flow reactor or a back-mixed reactor. Space time yield (STY) is defined herein to refer to the amount of grams of THF/kilogram catalyst/hour. Activity is defined herein to refer to the percent 30 acid converted at a given hold up time in a plug-flow reactor. Another important area subject to improvement is the preferential production of THF using catalysts that give both high selectivity and high space time yield. Such improvements are of great 35 commercial significance since they allow for the more

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economical production of THF which is an item of commerce with a plurality of uses. For example, tetrahydrofuran is a useful solvent for high polymers, such as polyvinyl chloride and as a monomer in 5 polyether polyols.

It has been discovered in the present invention that the process for making tetrahydrofuran in a back-mixed or plug-flow reactor using a highly active polometallic palladium-rhenium catalytic 10 composite including one or more metals selected from rhodium, cobalt, platinum, ruthenium, iron, thulium, cerium, yttrium, neodymium, aluminum, praesodymium, holmium, copper, samarium, europium, hafnium, manganese, vanadium, chromium, gold, terbium, 15 lutetium, nickel, scandium and niobium produces high space time yields of THF while maintaining high selectivity in a back mixed reactor or produces a high acid conversion in a plug flow reactor.

It has also been discovered in the present 20 invention that, in the continuous manufacture and removal by vapor take off of THF under back-mixed conditions with a highly active catalyst in an aqueous medium, maintaining the concentration of carboxylic acids within a predetermined range results in high 25 selectivity to THF with very little over reduction and surprisingly little loss in catalyst activity.

SUMMARY OF THE INVENTION

According to the present invention a 30 hydrogenatable precursor such as maleic acid, maleic anhydride, fumaric acid, succinic acid, succinic anhydride, malic acid, or mixtures thereof, i.e., these precursors can be described as dicarboxylic acids, or anhydrides, or mixtures of said acids and/or 35 anhydrides, is reacted with hydrogen in a back-mixed

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reactor or in a plug flow reactor at a temperature of about 150°C to 300°C at a pressure of about 1000 to 3000 psig in the presence of a novel tri- or polymetallic catalytic composite comprising a combination of a catalytically effective amount of palladium, rhenium and one or more metals (M), i.e., a metal component selected from rhodium, cobalt, platinum, ruthenium, iron, thulium, cerium, yttrium, neodymium, aluminum, praesodymium, holmium, copper, samarium, europium, hafnium, manganese, vanadium, chromium, gold, terbium, lutetium, nickel, scandium and niobium deposited on a support such as an activated, porous carbon carrier with a surface area in excess of about 650 m²/g or a refractory oxide carrier, e.g., alumina, zirconia, titania, hafnium oxide, silica or barium carbonate and the like, to produce high space time yields of THF while maintaining high selectivity in a back mixed reactor or to produce high acid conversion in a plug flow reactor. The polymetallic catalytic composites of this invention consist by total weight of: (1) from about 0.1 to 10 weight percent of a palladium component; (2) from about 1 to 20 weight percent of a rhenium component; and, (3) from about 0.01 to 1.0 weight percent of the metal component with the remaining weight comprising either an activated, porous carbon carrier or a refractory oxide carrier.

In another aspect of this invention, a hydrogenatable precursor is reacted on a continuous basis in an aqueous medium with hydrogen in a back-mixed reactor at a temperature of about 150°C to 300°C at a pressure of about 1000 to 3000 psig in the presence of a suitable hydrogenation catalyst with continuous THF removal by vapor take off, and the

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concentration of acid in the reaction mixture is maintained within a predetermined range.

DETAILED DESCRIPTION OF THE INVENTION

Catalyst and Preparation

5 One aspect of the invention relates to a novel tri- or polymetallic catalytic composite consisting essentially of a combination of: (1) a catalytically effective amount of palladium (Pd); (2) 10 a catalytically effective amount of rhenium (Re); and, (3) a catalytically effective amount of one or more metals (M), i.e., a metal component selected from 15 rhodium (Rh), cobalt (Co), platinum (Pt), ruthenium (Ru), iron (Fe), thulium (Tm), cerium (Ce), yttrium (Y), neodymium (Nd), aluminum (Al), praesodymium (Pr), holmium (Ho), copper (Cu), samarium (Sm), europium (Eu), hafnium (Hf), manganese (Mn), vanadium (V), chromium (Cr), gold (Au), terbium (Tb), lutetium (Lu), nickel (Ni), scandium (Sc) and niobium (Nb) deposited 20 on a support. The tri- or polymetallic catalytic composite consists essentially of about 0.1 to 10 weight percent of palladium, about 1 to 20 weight percent of rhenium and about 0.01 to 1.0 weight percent of the metal or metals M by total weight. 25 It is the addition of the metal or metals M that unexpectedly improves catalytic performance. Suitable supports include activated, porous carbons and refractory oxide carriers, e.g., alumina, zirconia, titania, hafnium oxide, silica or barium carbonate and 30 the like. The preferred carrier is an activated, porous carbon carrier. Suitable carbon supports have a surface area in excess of about $650 \text{ m}^2/\text{g}$ (measured using standard N_2 BET techniques), typically in excess of about $1000 \text{ m}^2/\text{g}$, preferably in excess of about $1500 \text{ m}^2/\text{g}$. The catalyst carbon support is fine powder 35

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particles for use in a slurry reactor or larger support granules for use in a fixed bed reactor.

The tri- or polymetallic catalytic composite of this invention can be prepared in any one of a number of different methods known in the art. However, a preferred step in the method for preparing said catalyst involves sequential deposition of the palladium component and the rhenium component as described in greater detail in U.S. Patent 4,609,636, the teachings of which are incorporated herein by reference. For example, a method for preparing said catalyst includes, in sequence, the steps of:

- (a) impregnating a carbon support with a solution containing sources of the metal M and palladium and removing the solvent;
- (b) drying the metal M and palladium impregnated carbon at a temperature in the range of from 100°C to 500°C, under reducing conditions for about 0.5 to 24 hours;
- (c) applying to the metal M and palladium impregnated carbon a source of rhenium in solution and removing the solvent to form said catalyst; and
- (d) drying the metal M/palladium/rhenium impregnated carbon at a temperature in the range of from 100°C to 500°C, under reducing conditions for about 0.5 to 24 hours.

It will be appreciated by those skilled in the art that variants of this method in which the source of metal (M) is applied to the support and reduced prior to the addition of the palladium, after the addition of the palladium, after the addition of the rhenium or simultaneously with the rhenium can also be officially employed to prepare the catalysts of this invention. This is illustrated by Examples

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65-67 which show that a catalyst prepared by an alternate sequence of metal deposition (Rh deposited and reduced before Pd, Example 30) gives similar performance properties.

5 The solution containing the palladium compound is typically an aqueous medium containing an amount of palladium compound to yield a catalyst product with the requisite amount of palladium. The palladium compound is typically $PdCl_2$ and can also be, but is not limited to, a palladium compound such as $PdBr_2$, $Pd(NO_3)_2$, $Pd(C_2H_3O_2)_2$ (wherein $C_2H_3O_2$ denotes acetate), $Pd(C_5H_7O_2)_2$ (wherein $C_5H_7O_2$ denotes acetylacetone), and coordination compounds such as $(NH_3)_4PdCl_2$ or $(NH_4)_2PdCl_6$. The solution containing the rhenium compound is typically an aqueous one containing an amount of rhenium compound to yield a catalyst product with the requisite amount of rhenium. The rhenium compound is typically Re_2O_7 but can be perrhenic acid or a perrhenate of ammonium or of an alkali metal, K_2ReCl_6 , $(C_2H_3O_2)_2ReCl$, or $(NH_4)_2Re_2Cl_8$, etc. The solution containing the metal compounds M are typically aqueous and contain an amount of metal sufficient to yield a catalyst product with the requisite metal loading. By way of example, when the metal is rhodium, the rhodium compound is typically $RhCl_3 \cdot xH_2O$ but can also be a rhodium compound such as $RhBr_3 \cdot xH_2O$, $Rh_2(C_2H_3O_2)_4$, $Rh_6(CO)_{16}$, $Rh_4(CO)_{12}$, $(Rh(CO)_2Cl)_2$, $Rh(C_5H_7O_2)_3$ or $Rh(NO_3)_3 \cdot 2H_2O$, $Rh_2(SO_4)_3$, as well as salts thereof exemplified by Na_3RhCl_6 , and $(C_4H_9)_4NRh(CO)_2Cl_2$, and coordination compounds where Rh is ligated, for example by amines, halides, carboxylates, ca bon monoxide, etc., exemplified by $Rh(NH_3)_6Cl_3$. When the metal is iron, the iron compound is typically $FeCl_3 \cdot 6H_2O$ but can also be an iron compound such as $FeCl_2 \cdot xH_2O$, $FeBr_2$,

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$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Fe}(\text{SO}_4) \cdot 7\text{H}_2\text{O}$, $\text{Fe}_2(\text{SO}_4)_3$, $\text{Fe}(\text{C}_5\text{H}_7\text{O}_2)_3$, $(\text{C}_5\text{H}_5)_2\text{Fe}$ (wherein C_5H_5 denotes cyclopentadienyl), $\text{Fe}(\text{CO})_5$, $\text{Fe}_2(\text{CO})_9$, as well as salts and coordination compounds thereof. When the metal is cobalt, the

5 cobalt compound is typically $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ but can also be a cobalt compound such as $\text{CoBr}_2 \cdot x\text{H}_2\text{O}$, $\text{Co}(\text{OH})_2$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2$, Co_3O_4 , $\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_2$, $\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_3$, $\text{Co}_2(\text{CO})_8$, coordination compounds such as $\text{Co}(\text{NH}_3)_6\text{Cl}_3$, and salts such as

10 $\text{Co}(\text{ClO}_4)_2$. When the metal is platinum, the platinum compound is typically $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, but can also be a platinum compound such as PtCl_2 , Na_2PtCl_4 , PtCl_4 , PtBr_2 , PtBr_4 , H_2PtBr_6 , $\text{H}_2\text{Pt}(\text{OH})_6$, $\text{Pt}(\text{C}_5\text{H}_7\text{O}_2)_2$, coordination compounds such as $(\text{NH}_4)_2\text{PtCl}_4$, $(\text{C}_2\text{H}_8\text{N}_2)_3\text{PtCl}_4$, or $(\text{NH}_3)_4\text{Pt}(\text{NO}_3)_2$, and organometallic precursors such as $(\text{n-C}_4\text{H}_9)_4\text{N}\text{PtBr}_3(\text{CO})$. When the metal is ruthenium, the ruthenium compound is

15 typically $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, but can also be a ruthenium compound such as $\text{RuBr}_3 \cdot x\text{H}_2\text{O}$, $\text{RuNO}(\text{NO}_3)_3$, $\text{RuO}_2 \cdot x\text{H}_2\text{O}$, $\text{Ru}(\text{C}_5\text{H}_7\text{O}_2)_3$, $\text{Ru}_2(\text{C}_2\text{H}_3\text{O}_2)_4\text{Cl}$, coordination compounds such as $\text{Ru}(\text{NH}_3)_5\text{Cl}_3$ and $(\text{NH}_4)_2\text{Ru}(\text{H}_2\text{O})\text{Cl}_5$, $(\text{NH}_4)_2\text{RuCl}_6$, and organometallic compounds such as $\text{Ru}_3(\text{CO})_{12}$. When the metal is thulium, the thulium compound is

20 typically $\text{TmCl}_3 \cdot 7\text{H}_2\text{O}$, but can also be a thulium compound such as $\text{TmBr}_3 \cdot x\text{H}_2\text{O}$, TmF_3 , TmI_3 , Tm_2O_3 , $\text{Tm}(\text{C}_2\text{H}_3\text{O}_2)_3 \cdot x\text{H}_2\text{O}$, $\text{Tm}(\text{C}_5\text{H}_7\text{O}_2)_3$, $\text{Tm}_2(\text{CO}_3)_3 \cdot x\text{H}_2\text{O}$, and $\text{Tm}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$. When the metal is cerium, the cerium compound is typically $\text{CeCl}_3 \cdot x\text{H}_2\text{O}$, but can also be a cerium compound such as $\text{CeBr}_3 \cdot 6\text{H}_2\text{O}$, CeF_3 , CeI_3 , $\text{Ce}_2(\text{C}_2\text{H}_3\text{O}_2)_3 \cdot 3\text{H}_2\text{O}$, $\text{Ce}_2(\text{CO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ce}(\text{C}_5\text{H}_7\text{O}_2)_3$, as well as salts such as $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$. When the metal is yttrium, the yttrium compound is

25 typically $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$, but can also be a yttrium compound such as $\text{YBr}_3 \cdot x\text{H}_2\text{O}$, YF_3 , Y_2O_3 , $\text{Y}(\text{C}_2\text{H}_3\text{O}_2)_3 \cdot 4\text{H}_2\text{O}$, $\text{Y}(\text{C}_5\text{H}_7\text{O}_2)_3$, $\text{Y}(\text{C}_3\text{H}_7\text{O})_3$, $(\text{C}_5\text{H}_5)_3\text{Y}$,

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$Y_2(CO_3)_3 \cdot 3H_2O$, and $Y(NO_3)_3 \cdot 6H_2O$. When the metal is neodymium, the neodymium compound is typically $NdCl_3 \cdot 6H_2O$, but can also be a neodymium compound such as $NdBr_3 \cdot xH_2O$, NdF_3 , NdI_3 , Nd_2O_3 , $Nd(C_2H_3O_2)_3 \cdot H_2O$, 5 $Nd(C_5H_7O_2)_3$, $Nd(NO_3)_3 \cdot 6H_2O$ and $Nd_2(CO_3)_3 \cdot xH_2O$. When the metal is aluminum, the aluminum compound is typically $AlCl_3 \cdot 6H_2O$, but can also be an aluminum compound such as $AlCl_3$, $AlBr_3$ and hydrates, AlF_3 and hydrates, AlI_3 , $Al(OH)_3$, $Al(C_3H_7O)_3$ (wherein C_3H_7 is 10 isopropoxide), $Al(C_5H_7O_2)_3$, and $Al(NO_3)_3 \cdot 9H_2O$. When the metal is praesodymium, the praesodymium compound is typically $PrCl_3 \cdot 7H_2O$, but can also be a praesodymium compound such as $PrBr_3$ and hydrates, PrF_3 , PrI_3 , Pr_6O_{11} , $Pr(C_2H_3O_2)_3 \cdot 3H_2O$, $Pr(C_5H_7O_2)_3$, 15 $Pr_2(CO_3)_3 \cdot 8H_2O$ and $Pr(NO_3)_3 \cdot 6H_2O$. If the metal is holmium, the holmium compound is typically $HoCl_3 \cdot 6H_2O$, but can also be a holmium compound such as $HoBr_3$ and hydrates, HoF_3 , HoI_3 , Ho_2O_3 , $Ho(C_5H_7O_2)_3$, $Ho(C_2H_3O_2)_3 \cdot xH_2O$, $Ho_2(CO_3)_3 \cdot xH_2O$ and $Ho(NO_3)_3 \cdot 5H_2O$. 20 The M precursor can be any M compound with properties suitable for the catalyst preparation, e.g., soluble in the solvent of choice. Suitable compounds include oxides, carbonates, alkoxides, -diketonates, halides, nitrates, sulfates, hydroxides, carboxylates, 25 carbonyls, coordination compounds and combinations of the above as well as solvates and salts thereof. A preferred M compound is of the general formula $MCl_x \cdot xH_2O$.
The preparation of the catalyst composite 30 may be carried out in the presence of Group IA or IIA metals, which may be present in the carbon as obtained or may be added. For example, the beneficial effect of the addition of potassium is shown in Example 70. It is believed that addition of potassium to the slurry catalyst of the present invention can be 35

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beneficially employed in a slurry reactor. The fixed bed catalyst support carbon contains potassium as obtained.

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Catalytic Process for Preparing THF

Another aspect of the present invention involves the catalytic process for preparing THF, employing the tri- or polymetallic catalytic composite described above, in a back-mixed reactor to achieve a 10 high space time yield, e.g., in excess of about 280 g THF/kg catalyst/hr in a back-mixed reactor while maintaining high selectivity, e.g., up to about 90%. Alternatively, the process can be carried out in a plug flow reactor with a catalyst of the present 15 invention exhibiting high activity, e.g., in excess of 58% acid conversion of a 5% by weight maleic acid feed at 250°C, 2000 psig total pressure and a contact time of 0.016 hour. More preferred composites employed in the process are those wherein the metal component is 20 selected from rhodium, cobalt, platinum, ruthenium, iron, thulium, cerium, yttrium, neodymium, aluminum, praesodymium and holmium.

The hydrogenatable precursors, i.e., starting reactants useful for carrying out the 25 invention are, for example, maleic acid, maleic anhydride, fumaric acid, succinic acid, succinic anhydride, malic acid, or mixtures thereof. These precursors can be described as dicarboxylic acids, or anhydrides, or mixtures of said acids and/or anhydrides. Preferred hydrogenatable precursors 30 include maleic acid and malic anhydride. For example, using these precursors in aqueous solution, the process is believed to proceed in a stepwise manner with maleic acid (MAC) first being reduced to 35 succinic acid (SAC) which is further reduced to

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reduced directly to THF, but is also reduced to BDO which is finally dehydrated to THF. By products include alcohols (1-propanol (PrOH) and 1-butanol (BuOH)) and alkanes (primarily butane, methane). It
5 will be appreciated by those skilled in the art that the process of this invention is equally applicable to the production of 3-methyltetrahydrofuran. Suitable hydrogentable precursors to 3-methylTHF include, but are not limited to, itaconic acid, itaconic anhydride, citraconic acid, citraconic anhydride, mesaconic acid, citric acid and aconitic acid. Itaconic acid is a preferred precursor due to cost and ease of reduction. It is further recognized that analogous precursors to other substituted THFs, such as 3-ethylTHF and
10 15 3-propylTHF can be beneficially employed in the process of this invention.

Production of THF includes the hydrogenation of the hydrogentable precursor in an aqueous or organic solvent medium, i.e., the precursor solution
20 is reacted with hydrogen in a back-mixed reactor or in a plug flow reactor. A preferred solvent for the process of this invention is water. The hydrogenation conditions include a reaction temperature in the range of about 150°C to 300°C, preferably about 250°C and a
25 hydrogen pressure of about 1000 to 3000 psig, preferably about 2000 psig, a hydrogen spacetime of about 1 to 14 minutes and a liquid contact time of about 0.5 to 7 hours in the presence of the tri- or polymetallic catalytic composite described above. The
30 hydrogenation of this invention can be run using conventional apparatus and techniques in a back-mixed or plug flow reactor. Hydrogen is fed continuously, generally in considerable stoichiometric excess. Unreacted hydrogen can be returned to the reactor as a
35 recycled stream. The precursor solution, e.g., maleic

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acid-water solution, is fed continuously at concentrations ranging from dilute solutions to near the maximum solubility level; typically the concentration is between about 30 to 40 weight percent. The catalyst carbon support is fine powder particles for use in a slurry reactor or larger support granules for use in a fixed bed reactor. The amount of catalyst required will vary widely and is dependent upon a number of factors such as reactor size and design, contact time and the like.

One method for carrying out the invention is in a plug flow reactor as described in greater detail in the examples. The selectivity was a measure of what percent of the exit stream is composed of THF, BDO and GBL. The highly active catalysts of this invention, when tested in a plug flow reactor, typically exhibit higher activity, and comparable selectivity, than a similarly prepared bimetallic Pd,Re/C catalyst. The loss of selectivity observed in some cases may be caused by over hydrogenation. If the catalyst is highly active but unselective at a certain temperature, decreasing its activity by lowering the temperature increases selectivity. Operating at lower temperatures can be an advantage in itself.

A preferred method of preparing THF is in a back-mixed reactor such as, for example, a continuous slurry reactor. It has been discovered in the present invention that the higher activity of the tri- or polymetallic catalytic composite described above can be most effectively utilized to give high STY and selectivity to THF in this type of reactor. While this reactor configuration results in a high concentration of aqueous carboxylic acids in the reactor, it has surprisingly been found that highly

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active palladium/rhenium-on-carbon catalysts, such as those described herein and in U. S. Patent 4,609,636, still perform well in a reaction mixture containing high concentration of acid. One major advantage of 5 the back-mixed reactor, which is particularly well-suited for producing THF from maleic acid, is vapor take off of THF, i.e., the THF can be purged from the reactor shortly after being formed, thus minimizing "over-hydrogenation", i.e., further 10 reduction of the desired THF product, to form less desirable alcohols and alkanes. A second advantage of the back-mixed reactor is that acid in the feed is distributed throughout the reaction mass, and is thus 15 available to catalyze the last step in the maleic acid to THF sequence, i.e., the ring closing of BDO to THF. This is of critical importance since it has been found that the BDO is also subject to over hydrogenation and a rapid conversion of BDO to THF serves to minimize 20 yield losses due to over reduction of the BDO. It will be appreciated by those skilled in the art that these two features of a back-mixed reactor contribute to the ability to use the catalyst of higher activity without loss in selectivity. Alternatively, a fixed 25 bed reactor with adequate recycle such that it approximates a back-mixed reactor can be used to carry out the invention.

Tetrahydrofuran and 1,4-butanediol are the products produced by the process of this invention in a plug flow reactor or in a back-mixed reactor. The 30 catalysts and processes of this invention are particularly well suited for the manufacture of THF. Another aspect of the invention is the production of THF in an essentially back-mixed reactor using a continuous process which provides definite advantages 35 for separation and recovery of THF, for example: (1)

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THF and over reduced by products are volatile and can be distilled out of a back mixed reactor as they are formed and, if necessary, the THF further purified using conventional procedures; (2) the maleic acid starting material and the intermediates (up to and including BDO) are less volatile and tend to remain behind in the reactor; and (3) small amounts of THF precursors or intermediates, such as GBL, which are swept out with the THF can be separated and recycled to the reactor. In the continuous hydrogenation process of this invention, the BDO and THF are initially produced and the relative amounts obtained are dependent upon the nature of the catalyst employed as well as other factors such as those described in U.S. patent 4,609,636. The conversion of BDO produced to THF does not require further hydrogenation, but only an acid-catalyzed ring closure. This conversion is readily achieved in a back mixed reactor where the concentration of the carboxylic acids in the reaction mixture is maintained within a predetermined range, e.g., between about 1% and 10% by weight (calculated as succinic acid) of the reaction mixture. Preferably the concentration of carboxylic acids in the reaction mixture is maintained in excess of about 3% by weight of the reaction mixture. Better STY and selectivity is obtained above 3% by weight while fewer operational problems associated with acid solidification in process equipment are encountered below about 10%, typically about 8% by weight. This continuous process is particularly well suited for use with certain highly active hydrogenation catalysts which comprise a bi-, tri-, or polymetallic catalytic composite of fine metallic particles on an activated porous carbon support. For example, catalysts for use in this continuous process are comprised of, by total weight,

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from about 0.1 to 10 weight percent of palladium, about 1 to 20 weight percent of rhenium and optionally from about 0.01 to 1.0 weight percent of a component containing one or more of the metals selected from 5 rhodium, cobalt, platinum, ruthenium, iron, thulium, cerium, yttrium, neodymium, aluminum, praesodymium, holmium, copper, samarium, europium, hafnium, manganese, vanadium, chromium, gold, terbium, lutetium, nickel, scandium and niobium on a carbon 10 support having a surface area in excess of about 1000 m²/g. A preferred hydrogenatable precursor for use in this continuous process is aqueous maleic acid. In the continuous process of the present invention, the required acid is provided by maleic, succinic, and to 15 a lesser extent, other acids distributed throughout the reaction mixture in the back-mixed reactor. Thus, by controlling acid levels according to the process of this invention, high selectivity to THF can be obtained regardless of the relative amounts of BDO and 20 THF initially produced with very little over reduction and surprisingly little loss in catalyst activity. It will be appreciated by those skilled in the art that the continuous process of this invention is equally applicable to the production of 3-methyltetrahydro- 25 furan. Suitable hydrogentable precursors to 3-methyl-THF include, but are not limited to, itaconic acid, itaconic anhydride, citraconic acid, citraconic anhydride, mesaconic acid, citric acid and aconitic acid. Itaconic acid is a preferred precursor due to 30 cost and ease of reduction. It is further recognized that analogous precursors to other substituted THFs, such as 3-ethylTHF and 3-propylTHF can be beneficially employed in the continuous process of this invention.

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The following examples serve to illustrate the invention, but are not intended to limit the scope of the invention.

5

EXAMPLE 1

An example of a preparation of a catalyst suitable for use in a slurry reactor is presented. Note that the items in parentheses refer to the parameter headings in Table 1. The remaining 10 preparations of slurry catalysts, i.e., Examples 2-4 were done in the same way; the parameters used in the preparation of Examples 2-4 are listed in Table 1.

This example describes the preparation of a Rh+Pd,Re/C trimetallic catalytic composite of the 15 present invention, suitable for use in a slurry reactor (type). The notation M+Pd,Re/C is meant to imply that M and Pd were codeposited and reduced followed by Re deposition and reduction.

0.24 g $\text{RhCl}_3 \cdot \text{H}_2\text{O}$ (M precursor) containing 20 0.10 g Rh(Wt M) was dissolved in 115 ml H_2O . 3.30 ml (vol 1 = 115+3.3) $\text{PdCl}_2 \cdot \text{HCl}$ stock solution containing 0.5 g Pd (Wt Pd) was added. The solution was added to 25 50g (wt C1) Darco KBB® carbon, commercially available, and the resulting slurry was stirred occasionally over a 3 hour period at room temperature. The slurry was dried overnight at 115°C. The Rh,Pd/C powder was recovered and then reduced at 300°C in flowing H_2 -He (1:1) for eight hours. The reduced powder was cooled to 30 50°C, purged with He, cooled to room temperature in flowing He, and then passivated 30 minutes in flowing 1% O₂ in N₂. A solution was prepared by adding 13.1 ml of a $\text{Re}_2\text{O}_7 \cdot \text{H}_2\text{O}$ stock solution containing 1.03 g Re (wt Re) to 77ml (vol 2=13.1+77) H_2O . This solution was added to 36.4 g (wt C₂) of reduced Rh,Pd/C and 35 stirred occasionally for 3 hours at room temperature.

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The Rh,Pd,Re/C sample was dried, reduced and passivated as above. Nominal loadings are 0.2% Rh(% M), 1.0% Pd(% Pd), and 2.8% Re(% Re). Nominal loading is defined as 100*wt metal/wt support

5 composite(support + any metals previously deposited).

Example 5

This example describes the preparation of a trimetallic Rh+Pd,Re/C catalytic composite of the present invention suitable for use in the fixed bed reactor. Note that the items in parentheses refer to the parameter headings in Table 1. The preparations of fixed bed catalysts of Examples 5-12 were done in the same way; the parameters used in the preparation of Examples 5-12 are listed in Table 1.

0.064 g $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ (M precursor) containing 0.027 g Rh (Wt M) was added to 0.65 ml $\text{PdCl}_2\text{-HCl}$ stock solution containing 0.099 g Pd (Wt Pd). 18 ml H_2O (vol 1 = 0.65+18) was added and mixed well. The solution was added to 10 g (Wt Cl) Calgon PCB® 12x30 carbon (commercially available), which had been calcined at 400°C for two hours in air and the resulting slurry was stirred occasionally over a 3 hour period at room temperature. The slurry was dried overnight at 115°C.

The Rh, Pd/C powder was recovered and then reduced at 300°C in flowing $\text{H}_2\text{-He}$ (1:1) for eight hours. The reduced powder was cooled to 50°C, purged with He, cooled to room temperature in flowing He, and then passivated 30 minutes in flowing 1% O_2 in N_2 . A solution was prepared by adding 3.76 ml of a $\text{Re}_2\text{O}_7\text{-H}_2\text{O}$ stock solution containing 0.29 g Re (Wt Re) to 10 ml H_2O (vol 2 = 3.76+10). This solution was added to 8.0 g of reduced Rh, Pd/C (Wt C₂) and stirred occasionally for 3 hours at room temperature. The Rh+Pd, Re/C sample was dried, reduced and passivated as above. Nominal

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loadings are 0.3% Rh(% M), 1.0% Pd(% Pd), and 3.6% Re(% Re).

5 The catalysts of Examples 13-29 were prepared similarly, but a slightly different reduction protocol was used. The preparation of Example 13 is described in detail to indicate these slight differences. The preparation parameters for Examples 13-29 are listed in Table 1.

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Example 13

0.22 g $TmCl_3 \cdot 7H_2O$ (M precursor) containing 0.093 g Tm (Wt M) was added to a solution of 1.00 ml $PdCl_2 \cdot HCl$ stock solution containing 0.147 g Pd (Wt Pd) in 29 ml H_2O (vol 1 = 1.00+29) and mixed well. 15 g (Wt Cl) Calgon PCB® 12x30 carbon (commercially available) which had been calcined at 400°C in air for 2 hours, was added to the solution and the resulting slurry was stirred occasionally over a 3 hour period at room temperature. The slurry was dried overnight at 115°C. 20 The Tm, Pd/C powder was recovered and then reduced at 300°C in flowing H_2 -He (3:97) for 5.8 hours. The reduced powder was purged with He at 300°C for 0.5 hour, cooled to room temperature overnight (>5 hours) in flowing He. A solution was prepared by adding 6.5 ml of a $Re_2O_7 \cdot H_2O$ stock solution containing 0.52 g Re (Wt Re) to 19.5 ml H_2O (vol 2 = 6.5+19.5). To this 25 solution was added 13.0 g of reduced Tm, Pd/C (Wt C_2) and stirred occasionally for 3 hours at room temperature. The Tm+Pd, Re/C sample was dried and 30 reduced as above. Nominal loadings are 0.6% Tm (% M), 1.98% Pd (% Pd), and 4.0% Re (% Re).

35 The Rh, Pd, Re/C catalyst of Example 30 was prepared using a different sequence of metal deposition from previous examples. Rh was deposited on the carbon support and reduced. Pd was next

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deposited and reduced, and then Re was deposited and reduced.

Example 30

5 0.094 g $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ containing 0.040 g Rh was added to 36ml H_2O and mixed well. To this solution was added 20g of Calgon PCB® 12x30 carbon (commercially available) which had been calcined at 400°C in air for 2 hours, and the resulting slurry was 10 stirred occasionally over a 3 hour period at room temperature. The slurry was dried overnight at 115°C. The Rh/C powder was recovered and then reduced at 300°C in flowing H_2 -He (1:1) for eight hours. The reduced powder was cooled to 50°C, purged with He, 15 cooled to room temperature in flowing He, and then passivated 30 minutes in flowing 1% O_2 in N_2 . A solution was prepared by adding 1.12 ml of a $\text{PdCl}_2\text{-HCl}$ stock solution containing 0.17 g Pd to 30 ml H_2O . To this solution was added 16.8 g of reduced Rh/C and 20 stirred occasionally for 3 hours at room temperature. The Rh,Pd/C sample was dried, reduced and passivated as above. A solution was prepared by adding 4.80 ml of a $\text{Re}_2\text{O}_7\text{-H}_2\text{O}$ stock solution containing 0.38 g Re to 15 ml H_2O . To this solution was added to 8.0 g of 25 reduced Rh,Pd/C and stirred occasionally for 3 hours at room temperature. The Rh,Pd,Re/C sample was dried, reduced and passivated as above. Nominal loadings are 0.2% Rh, 1.0% Pd, and 4.8% Re.

30

Comparative Example A

Preparation of a Bimetallic Pd,Re/C Slurry Catalyst
6.30 ml $\text{PdCl}_2\text{-HCl}$ stock solution containing 0.96 g Pd was added to 224 cc water. The solution was added to 77g Darco KBB® carbon, 35 commercially available, and the resulting slurry was

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stirred occasionally over a 3 hour period at room temperature. The slurry was dried overnight at 115°C. The Pd/C powder was recovered and then reduced at 300°C in flowing H₂-He (1:1) for eight hours. The 5 reduced powder was cooled to 50°C, purged with He, cooled to room temperature in flowing He, and then passivated 30 minutes in flowing 1% O₂ in N₂. A solution was prepared by adding 36.3 ml of a Re₂O₇-H₂O stock solution containing 2.78g Re to 200ml H₂O. This 10 solution was added to 71.0g of reduced Pd/C and stirred occasionally for 3 hours at room temperature. The Pd,Re/C sample was dried, reduced and passivated as above. Nominal loadings are 1.25% Pd and 3.9% Re.

15

Comparative Example B

Preparation of a Bimetallic Pd,Re/C
Fixed Bed Catalyst

6.80 ml PdCl₂-HCl stock solution containing 1.01 g Pd was added to 172cc water and mixed well. 20 The solution was added to 100g Calgon PCB® 12x30 carbon (commercially available) which had been calcined at 400°C in air for 2 hours and the resulting slurry was stirred occasionally over a 3 hour period at room temperature. The slurry was dried overnight 25 at 115°C. The Pd/C powder was recovered and then reduced at 300°C in flowing H₂-He (1:1) for eight hours. The reduced powder was cooled to 50°C, purged with He, cooled to room temperature in flowing He, and then passivated 30 minutes in flowing 1% O₂ in N₂. A 30 solution was prepared by adding 45.1 ml of a Re₂O₇-H₂O stock solution containing 3.60 g Re(Wt Re) to 116 ml H₂O. This solution was added to 90 g of reduced Pd/C and stirred occasionally for 3 hours at room temperature. The Pd,Re/C sample was dried, reduced

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and passivated as above. Nominal loadings are 1.0% Pd and 4.0% Re.

Comparative Example C

5 Preparation of a Bimetallic Pd,Re/C
Slurry Catalyst Containing Potassium
1.91g KCl was dissolved in 230cc DI water
and mixed well. This mixture was added to 100g Darco
KBB® carbon, commercially available, and stirred
occasionally over a 3 hour period at room temperature.
10 The slurry was dried overnight at 115°C. 5.4 ml
PdCl₂-HCl stock solution containing 0.82 g Pd was
added to 192cc water and mixed well. The solution was
added to 85.1g K/C and the resulting slurry was
15 stirred occasionally over a 3 hour period at room
temperature. The slurry was dried overnight at 115°C.
The K,Pd/C powder was recovered and then reduced at
300°C in flowing H₂-He (1:1) for eight hours. The
reduced powder was cooled to 50°C, purged with He,
20 cooled to room temperature in flowing He, and then
passivated 30 minutes in flowing 1% O₂ in N₂. A
solution was prepared by adding 36.2 ml of a Re₂O₇-H₂O
stock solution containing 2.84g Re to 200ml H₂O. This
solution was added to 70.7g of reduced K,Pd/C and
25 stirred occasionally for 3 hours at room temperature.
The K,Pd,Re/C sample was dried, reduced and passivated
as above. Nominal loadings are 1.0%K, .96% Pd and
4.0% Re.

30 Catalyst Performance in a Back-Mixed Reactor

The catalyst fo. a back-mixed reactor was
tested by charging 7-15 g (dry basis) of slurry
catalyst in 150 ml water to a 300 ml Hastaloy C
autoclave, equipped with an agitator, a thermocouple,
35 feed lines for hydrogen and maleic acid, and an exit

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line through which the product was swept out with the excess hydrogen and water. The catalyst was activated by heating at 250°C under a 1000 ml/min hydrogen flow at 2000 psig for one hour. The maleic acid was fed as 5 a 40% by weight aqueous solution at feed rates ranging from 18 to 36 ml/min, and the reactor was maintained at 2000 psig and 250°C. The volatile products and water were swept out of the reactor at a rate controlled by the hydrogen feed rate. The hydrogen 10 feed rate was adjusted so that the amount of water carried out with the exiting hydrogen gas balances the amount of water added with the maleic acid feed and the amount produced by the reaction; the reactor level was maintained at 100-200cc. Note that in all cases a 15 very large excess of hydrogen was fed, compared to the amount consumed by the reaction; thus, the hydrogen feed rate does not affect catalyst performance.

Several different feed rates of maleic acid 20 were used in a catalyst test. Typically, the feed rate was increased from run to run until optimum performance was achieved. The reproducibility of this optimum performance was then checked over two or more runs at the same conditions.

A catalyst test was made up of several runs. 25 Typically, each run lasts 8-12 hours, with the reactor in steady state operation for 6-10 hours. The product composition data generated during steady state operation was averaged to give the average production rates(g/hr) of THF, BDO, GBL, PrOH, BuOH, and alkanes 30 (primarily butane and methane). The product composition data were measured in the following way. A portion of the volatilized product/water in the 35 exit gas stream is condensed and collected as "liquid product". The volume of the liquid product collected each hour was measured, and its composition analyzed

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using a calibrated gas chromatograph (GC) equipped with a flame ionization detector. The remaining uncondensed product(THF and alkanes) still in the exit gas stream was analyzed by measuring the gas flow rate, then analyzing the gas stream every two hours, using procedures similar to the one used for liquid analysis. The reactor contents are sampled every four hours and analyzed by GC and titration. The GC analysis was carried out using a Supelcowax 10 capillary column (30 m X 0.052 milliliter) which was maintained at 75°C for 5 minutes after injection and then heated at 10°C per minute to a final temperature of 200°C. The acid level in the mixture was measured by titration with sodium hydroxide and reported as % by weight of succinic acid. The combination of these three analyses permits calculation of the catalyst's performance (STY and selectivity) and the mass balance for each run.

25 Selectivity=(moles/hr of (THF(gas) + THF(liq) +
GBL(liq) + BDO(liq))) / (moles/hr of (THF(gas) +
THF(liq) + GBL(liq) + BDO(liq)+ PrOH(liq) + BuOH(liq)
+ alkane(gas)))

The maximum observed THF STY for the 1%, 4% Pd,Re/C slurry catalyst of comparative example A was 280 g THF/kg catalyst/hr. The trimetallic catalyst of this invention gave a THF STY in excess of 280 ; THF/kg catalyst/hr. The selectivity was a measure of what percentage of the exit stream was made up of THF, BDO and GBL. The addition of rhodium greatly imp. 'ved STY, while maintaining high selectivity.

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The back-mixed run results are summarized in Table 2.

Another aspect of the invention is control of the acid concentration in the reaction mixture within the range of about 1% and 10% by weight (calculated as succinic acid) of the reaction mixture. The bimetallic catalyst composite of Comparative Example A was run in several days in the backmixed reactor to demonstrate the beneficial effects of acid control. The results, listed in Table A, show the beneficial effects on STY and selectivity, e.g., increasing the acid concentration from about 3% to about 10% benefits STY and selectivity.

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Table A
CATALYST PERFORMANCE: BACKMIXED SLURRY REACTOR¹

	<u>Catalyst</u>	<u>Prepar- ation</u>	<u>Feed Rate²</u>	<u>Acid Conc.³</u>	<u>THF (STY)</u>	<u>Selec- tivity</u>
						(THF+ GBL+BDO)
20	Pd,Re/C	Ex.A	18 cc/hr	3.1%	216	83
			25	4.5	276	91
			31	8.0	280	91
			30	9.9	282	93

25 1 Hydrogenation of 40% maleic acid at 250°C in excess flowing H₂, 2000 psig total pressure.

2 Feed rate of 40% maleic acid/water in cc/hr.

3 Concentration of acid in the reactor, reported as wt% succinic acid, measured by acid-base titration.

30 The beneficial effects of increasing the concentration of acid in the reactor on STY and selectivity are apparent. Although not listed here, lower acid feed rates result in even lower acid concentration, STY and selectivity.

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Catalyst Performance in a Plug Flow Reactor

One method of preparing THF is liquid phase hydrogenation using conventional apparatus and techniques in a plug flow reactor as described in greater detail in U.S. Patent 4,609,636, the teachings of which are incorporated herein by reference.

5 The catalyst for a plug flow reactor was tested by charging 3 g. of catalyst to a 1/4 inch diameter Hastaloy U-tube reactor which was immersed in a heated sand bath for temperature control. The catalyst was activated by heating for one hour at 10 250°C in a 100 ml/min hydrogen flow at 2000 psig. Hydrogen and maleic acid were co-fed to one end of the reactor, and the liquid/gas stream exited from the 15 reactor through a pressure let-down valve which was set to control the pressure at the desired level. The excess gas was disengaged from the liquid in a chilled separator held at 90 psig pressure. In these experiments, the maleic acid was fed as a 5% aqueous 20 solution at flow rates ranging from 6 to 300 ml/hr. Hydrogen flow was maintained in large excess at 100 to 200 ml/min. The temperature was maintained at 250°C and pressure at 2000 psig.

Each catalyst was evaluated at four 25 different maleic acid feed rates to adequately map its performance characteristics. The gas and liquid was analyzed by GC as described above. Since neither maleic nor succinic acid is detected on the GC, the concentration of (maleic + succinic) acids in the 30 product was determined directly by acid-base titration and reported as weight % succinic acid.

The fixed bed performance data are summarized in Table 3. The percent of acid converted at a given hold up time is a measure of catalyst 35 activity. The selectivity to (THF + BDO + GBL) is the

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maximum observed in a fitted plot of selectivity vs contact time for the four different flow rates. The THF STY(g THF/kg catalyst/hr) is the curve maximum from a fitted plot of STY vs contact time for the four different flow rates.

The catalyst of this invention exhibited higher activity, and comparable selectivity, than the bimetallic Pd,Re/C catalyst of comparative Example B. The loss of selectivity observed in some cases was caused by "over-hydrogenation", i.e. reaction that goes beyond the desired THF product, to form alcohols and alkanes. Although the catalyst was too active at this temperature, resulting in over-hydrogenation, decreasing its activity by lowering the temperature increased selectivity, as shown in Table 4. Operating at lower temperatures can be an advantage in itself.

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TABLE 1
CATALYST PREPARATION

Ex.	Catalyst	Type	M Pre-cursor	wt (g) M/Pd/Re	wt (g) C1	vol 1/ vol 2 (cc)	wt (g) C2	Loading M/Pd/Re (%)
						vol 1/ vol 2 (cc)		
1	Rh+Pd, Re/C	slurry	RhCl ₃ *6H ₂ O	.10/.5/1.03	50	118/90	36.4	.2/1.0/2.8
2	Ru+Pd, Re/C	slurry	RuCl ₃ *3H ₂ O	.10/.5/1.03	50	118.3/	48	.2/1.0/2.1
3	Co+Pd, Re/C	slurry	CoCl ₃ *6H ₂ O	.12/.6/1.74	65	212.3/	59.2	.2/.9/2.9
4	Fe+Pd, Re/C	slurry	FeCl ₃ *6H ₂ O	.050/.50/50	154/59	21/6	1/1.0/4.0	
5	Rh+Pd, Re/C	fixed bed	RhCl ₃ *6H ₂ O	.027/.099/.29	10	19/14	8.0	.3/1.0/3.6
6	Ru+Pd, Re/C	fixed bed	RuCl ₃ *3H ₂ O	.026/.099/.29	10	19/14	8.0	.3/1.0/3.6
7	Co+Pd, Re/C	fixed bed	CoCl ₃ *6H ₂ O	.015/.099/.30	10	19/14	8.4	.15/1.0/3.6
8	Fe+Pd, Re/C	fixed bed	FeCl ₃ *6H ₂ O	.013/.099/.35	10	22/19	8.4	.15/1.0/4.2
9	Ni+Pd, Re/C	fixed bed	NiCl ₃ *6H ₂ O	.015/.099/.37	10	22/20	9.4	.15/.99/4.0
10	Aut+Pd, Re/C	fixed bed	AuCl ₂	.25/.505/1.92	50	90/87	48	.51/1.0/4.0
11	Pt+Pd, Re/C	fixed bed	H ₂ PtCl ₆ *6H ₂ O	.015/.099/.36	10	19/15	8.9	.15/1.0/4.0
12	Mn+Pd, Re/C	fixed bed	MnCl ₂ *6H ₂ O	.031/.145/.52	15	30/26	13	.20/1.0/4.0
13	Tm+Pd, Re/C	fixed bed	TmCl ₃ *7H ₂ O	.093/.147/.52	15	30/26	13	.60/.98/4.0
14	Ce+Pd, Re/C	fixed bed	CeCl ₃ *7H ₂ O	.030/.154/.52	15	29/26	13	.20/1.0/4.0
15	Y+Pd, Re/C	fixed bed	YCl ₃ *6H ₂ O	.047/.154/.52	15	29/26	13	.31/1.0/4.0
16	Nd+Pd, Re/C	fixed bed	NdCl ₃ *6H ₂ O	.076/.147/.52	15	30/26	13	.51/.98/4.0
17	Al+Pd, Re/C	fixed bed	AlCl ₃ *6H ₂ O	.030/.154/.52	15	30/27	13	.20/1.0/4.0
18	Pr+Pd, Re/C	fixed bed	PrCl ₃ *7H ₂ O	.076/.154/.52	15	29/26	13	.51/1.0/4.0
19	Ho+Pd, Re/C	fixed bed	HoCl ₃ *6H ₂ O	.083/.147/.52	15	30/26	13	.55/9.8/4.0
20	Cu+Pd, Re/C	fixed bed	CuCl ₃ *2H ₂ O	.030/.154/.52	15	30/26	13	.20/1.0/4.0
21	Sm+Pd, Re/C	fixed bed	SmCl ₃ *6H ₂ O	.082/.147/.52	15	29/26	13	.55/1.0/4.0
22	Eu+Pd, Re/C	fixed bed	EuCl ₃	.082/.147/.51	15	30/25	12.8	.55/.98/4.0
23	Hf+Pd, Re/C	fixed bed	HfOCl ₂	.096/.147/.51	15	29/25	12.8	.64/.98/4.0
24	V+Pd, Re/C	fixed bed	VCl ₃	.026/.147/.52	15	30/26	13	.18/1.0/4.0
25	Cr+Pd, Re/C	fixed bed	CrCl ₃ *6H ₂ O	.028/.151/.51	15	29/25	12.9	.19/1.0/4.0
26	Tb+Pd, Re/C	fixed bed	TbCl ₃	.084/.147/.52	15	30/26	13	.56/1.0/4.0
27	Lu+Pd, Re/C	fixed bed	LuCl ₃ *6H ₂ O	.094/.147/.52	15	30/26	13	.63/1.0/4.0
28	Sc+Pd, Re/C	fixed bed	ScCl ₃ *6H ₂ O	.025/.147/.52	15	29/26	13	.16/.98/4.0
29	Nb+Pd, Re/C	fixed bed	NbCl ₃	.044/.147/.50	15	30/25	12.6	.29/.98/4.0

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TABLE 2
CATALYST PERFORMANCE: BACK MIXED SLURRY REACTOR¹

5	EX.	CATALYST	PREPARATION	THF STY	SELECTIVITY
10	31	Pd, Re/C	Ex. A	280	90
	32	Rh+Pd, Re/C	Ex. 1	500	88-90
	33	Ru+Pd, Re/C	Ex. 2	350	88-90
	34	Co+Pd, Re/C	Ex. 3	430	90-92
	35	Fe+Pd, Re/C	Ex. 4	413	90

1 Hydrogenation of 40% maleic acid at 250°C in excess flowing H₂, 2,000 psig total pressure.

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TABLE 3
CATALYST PERFORMANCE: PLUG FLOW FIXED BED REACTOR¹

20	EX.	CATALYST	PREP.	ACID CONV. (2)	SELEC- TIVITY (3)	THF STY
25	36	Pd, Re/C	EX. B	58 (%) (4)	83 (%)	389
	37	Rh+Pd, Re/C	EX. 5	77.5	74	374
	38	Ru+Pd, Re/C	EX. 6	72 (4)	70	384
	39	Co+Pd, Re/C	EX. 7	81.6 (4)	85	484
	40	Fe+Pd, Re/C	EX. 8	93.5	82	658
30	41	Pt+Pd, Re/C	EX. 11	75.2	76	432
	42	Tm+Pd, Re/C	EX. 13	88	85	407
	43	Ce+Pd, Re/C	EX. 14	91	81	537
	44	Y+Pd, Re/C	EX. 15	88	85	383
	45	Nd+Pd, Re/C	EX. 16	85	86	425
35	46	Al+Pd, Re/C	EX. 17	81	79	393
	47	Pr+Pd/Re/C	EX. 18	86	85	461

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48	Ho+Pd, Re/C	EX. 19	83	85	404
49	Cu+Pd, Re/C	EX. 20	82	85	422
50	Sm+Pd, Re/C	EX. 21	81	84	355
51	Eu+Pd, Re/C	EX. 22	77	85	361
5	52	Hf+Pd, Re/C	EX. 23	73	80
	53	Mn+Pd, Re/C	EX. 12	74	83
	54	V+Pd, Re/C	EX. 24	75	82
	55	Cr+Pd, Re/C	EX. 25	84	81
	56	Au+Pd, Re/C	EX. 10	67(4)	84
	57	Tb+Pd, Re/C	EX. 26	69	84
10	58	Lu+Pd, Re/C	EX. 27	72	83.5
	59	Ni+Pd, Re/C	EX. 9	64	82
	60	Sc+Pd, Re/C	EX. 28	77	84.5
	61	Nb+Pd, Re/C	EX. 29	74	79
					491
15	1	Hydrogenation of 5% maleic acid at 250°C in excess flowing H ₂ , 2,000 psig total pressure.			
	2	Percent (maleic+succinic) acids converted at contact time of 0.016 hour.			
	3	Maximum percent selectivity to (THF + BDO + GBL).			
	4	Percent (maleic+succinic) acids converted at contact time of 0.016 hour; determined by difference, not by titration.			
20	1	Hydrogenation of 5% maleic acid at 250°C in excess flowing H ₂ , 2,000 psig total pressure.			
	2	Percent (maleic+succinic) acids converted at contact time of 0.016 hour.			
	3	Maximum percent selectivity to (THF + BDO + GBL).			
	4	Percent (maleic+succinic) acids converted at contact time of 0.016 hour; determined by difference, not by titration.			
25	1	Hydrogenation of 5% maleic acid at 250°C in excess flowing H ₂ , 2,000 psig total pressure.			
	2	Percent (maleic+succinic) acids converted at contact time of 0.016 hour.			
	3	Maximum percent selectivity to (THF + BDO + GBL).			
	4	Percent (maleic+succinic) acids converted at contact time of 0.016 hour; determined by difference, not by titration.			

TABLE 4

CATALYST PERFORMANCE VS.
TEMPERATURE: PLUG-FLOW FIXED BED REACTOR¹

30	EX.	CATALYST	RATION	PREPA-	TEMP	ACID	SELEC-	THF STY
						CONV (2)	TIVITY (3)	
35	62	Pd, Re/C	B	250	90(%)	83(%)	391	
	63	Pd, Re/C	B	225	77	88	240	
35	64	Pd, Re/C	B	275	89	76	493	
	65	Rh, Pd, Re/C	EX. 30	250	98	80	368	
	66	Rh, Pd, Re/C	EX. 30	250	100	80	388	

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67	Rh, Pd, Re/C	EX.30	200	76	84	142
68	Pd+Re, Rh	EX.5	250	97	74	374
69	Pd+Rh, Re	EX.5	200	79	84	124

5 1 Hydrogenation of 5% maleic acid in excess flowing H₂, 2,000 psig total pressure.
 2 Percent (maleic+succinic) acids converted at contact time of 0.03 hour; determined by difference, not by titration;
 10 3 Maximum percent selectivity to (THF + BDO + GBL).

TABLE B
 CATALYST PERFORMANCE: BACKMIXED SLURRY REACTOR¹

Example	Catalyst 70 K, Pd, Re/C	Preparation Ex.C	Acid Feed Rate ²
			24 cc/hr
			32
			31
Example	Acid Conc ³	THF STY	Selectivity THF+BDO+GBL
70	4.9%	285	85%
	6.4	355	85
	5.6	324	85

1 Hydrogenation of 40% maleic acid at 250C in excess flowing H₂, 2,000 psig total pressure.
 2 Feed rate of 40% maleic acid/water in cc/hr.
 3 Concentration of acid in the reactor, reported as weight % succinic acid, measured by acid-base titration.
 30 The beneficial effect of addition of potassium to the bimetallic Pd,Re/C catalyst are apparent- STY increased from 280 to approximately 335.

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CLAIMS

What is claimed:

5 1. A polometallic catalytic composite consisting essentially of a combination of a catalytically effective amount of fine particles of a

10 (a) palladium component;
(b) rhenium component; and
(c) one or more of a metal component selected from rhodium, cobalt, platinum, ruthenium, iron, thulium, cerium, yttrium, neodymium, aluminum, praesodymium and holmium

15 deposited on a support.

15 2. The polometallic catalytic composite of Claim 1 wherein the palladium component ranges from about 0.1 to 10 weight percent, the rhenium component ranges from about 1 to 20 weight percent and the metal component ranges from about 0.01 to 1.0 weight percent by total weight.

25 3. The polometallic catalytic composite of Claim 1 or Claim 2 wherein the support is selected from the group consisting essentially of an activated, porous carbon carrier having a surface area in excess of $650 \text{ m}^2/\text{g}$ or a refractory oxide carrier.

30 4. A hydrogenation catalyst consisting essentially of a polometallic catalytic composite of fine particles of palladium, rhenium and one or more of metal component selected from rhodium, cobalt, platinum, ruthenium, iron, thulium, cerium, yttrium, neodymium, aluminum, praesodymium, holmium, copper, samarium, europium, hafnium, manganese, vanadium,

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chromium, gold, terbium, lutetium, nickel, scandium and niobium on an activated porous carbon support having a surface area in excess of 650 m²/g and comprising about 0.1 to 10 weight percent of
5 palladium, about 1 to 20 weight percent of rhenium and about 0.01 to 1.0 weight percent of the metal component by total weight to achieve increased space time yield of product while maintaining high selectivity in a back mixed reactor or to achieve high
10 activity in a plug flow reactor.

5. The catalyst of Claim 4 wherein the metal component is selected from rhodium, cobalt, platinum, ruthenium, iron, thulium, cerium, yttrium, neodymium, aluminum, praesodymium and holmium.
15

6. A process for preparing tetrahydrofuran or substituted tetrahydrofuran from a hydrogenatable precursor, the process comprising contacting the hydrogenatable precursor with hydrogen at a temperature of about 150°C to about 300°C, and a pressure of about 1000 psig to about 3000 psig in the presence of a polymetallic catalytic composite comprising a combination of a catalytically effective amount of fine particles of a
20 (a) palladium component;
(b) rhenium component; and
(c) one or more of a metal component selected from rhodium, cobalt, platinum, ruthenium, iron, thulium, cerium, yttrium, neodymium, aluminum, praesodymium, holmium, copper, samarium, europium, hafnium, manganese, vanadium, chromium, gold, terbium, lutetium, nickel, scandium and
25 niobium
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deposited on a support.

7. The process of Claim 6 wherein the hydrogentable precursor is selected from itaconic acid, itaconic anhydride, citraconic acid, citraconic anhydride, mesaconic acid, citric acid and aconitic acid or mixtures thereof.

8. The process of Claim 6 wherein the metal component is selected from rhodium, cobalt, platinum, ruthenium, iron, thulium, cerium, yttrium, neodymium, aluminum, praesodymium and holmium.

9. The process of Claim 6 or Claim 8 wherein the support is selected from the group consisting of an activated, porous carbon carrier having a surface area in excess of $650 \text{ m}^2/\text{g}$ or a refractory oxide carrier.

10. The process of 9 wherein the palladium component comprises about 0.1 to 10 weight percent, the rhenium component comprises about 1 to 20 weight percent and the metal component comprises about 0.01 to 1.0 weight percent of the total weight.

11. The process of Claim 10 wherein the hydrogenatable precursor is selected from the group consisting of maleic acid, maleic anhydride, fumaric acid, succinic acid, succinic anhydride, malic acid, or mixtures thereof and is in an aqueous or organic solvent medium.

a.

12. The process of Claim 11 wherein the hydrogenatable precursor is selected from maleic acid and the solvent medium is water.

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13. A process for preparing tetrahydrofuran from an aqueous solution of maleic acid to achieve increased space time yield while maintaining high selectivity or exhibiting high activity, the process

5 comprising contacting said maleic acid with hydrogen at a temperature of about 150°C to about 300°C, and a pressure of about 1000 psig to about 3000 psig in the presence of a trimetallic catalytic composite comprising a combination of fine particles of a

10 (a) about 0.9-1.0 weight percent palladium component;

(b) about 2.1-4.5 weight percent rhenium component; and

(c) about 0.1 -0.6 weight percent of a metal component selected from rhodium, cobalt, platinum, ruthenium, iron, thulium, cerium, yttrium, neodymium, aluminum, praesodymium and holmium

15 deposited on an activated porous carbon support having a surface area in excess of 650 m²/g.

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14. A process for preparing tetrahydrofuran from a hydrogenatable precursor in a back-mixed reactor, the process comprising contacting the

25 hydrogenatable precursor with hydrogen at a temperature of about 150°C to about 300°C, and a pressure of about 1000 psig to about 3000 psig in the presence of a polymetallic catalytic composite comprising a combination of a catalytically effective amount of fine particles of a

30 (a) palladium component;

(b) rhenium component; and

(c) one or more of a metal component selected from rhodium, cobalt, platinum, ruthenium, iron, thulium, cerium, yttrium,

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neodymium, aluminum, praesodymium, holmium,
copper, samarium, europium, hafnium,
manganese, vanadium, chromium, gold,
terbium, lutetium, nickel, scandium and
5 niobium
deposited on a support.

15. A process for preparing tetrahydrofuran
from a hydrogenatable precursor in a plug flow
10 reactor, the process comprising contacting the
hydrogenatable precursor with hydrogen at a
temperature of about 150°C to about 300°C, and a
pressure of about 1000 psig to about 3000 psig in the
presence of a polometallic catalytic composite
15 comprising a combination of a catalytically effective
amount of fine particles of a
(a) palladium component;
(b) rhenium component; and
(c) one or more of a metal selected from one
20 or more of a metal component selected from
rhodium, cobalt, platinum, ruthenium, iron,
thulium, cerium, yttrium, neodymium,
aluminum, praesodymium, holmium, copper,
samarium, europium, hafnium, manganese,
25 vanadium, chromium, gold, terbium, lutetium,
nickel, scandium and niobium
deposited on a support.

30 16. The process of Claim 14 or Claim 15
wherein the hydrogenatable precursor is selected from
the group consisting essentially of maleic acid,
maleic anhydride, fumaric acid, succinic acid,
succinic anhydride, maleic acid or mixtures thereof.

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17. The process of Claim 16 further including the hydrogenatable precursor in an aqueous or organic solvent medium.

5 18. The process in Claim 13 or Claim 14 or Claim 15 wherein the support is an activated, porous carbon carrier having a surface area in excess of 650 m²/g or a refractory oxide carrier.

10 19. The process of Claim 14 further comprising an aqueous, continuous process wherein the hydrogenatable precursor is maleic acid and the concentration of carboxylic acids in the reaction mixture is 1% to 10% by weight of the reaction mixture 15 to accomplish high selectivity to tetrahydrofuran while minimizing over reduction of tetrahydrofuran.

20 20. An aqueous process for the manufacture of high purity tetrahydrofuran or substituted tetrahydrofuran by the continuous hydrogenation with vapor take off of tetrahydrofuran of a hydrogenatable tetrahydrofuran precursor selected from the group consisting of maleic acid, maleic anhydride, fumaric acid, succinic acid, succinic anhydride, malic acid, 25 and mixtures thereof, and itaconic acid, itaconic anhydride, citraconic acid, citraconic anhydride, mesaconic acid, citric acid, aconitic acid or mixtures thereof, in the presence of a suitable hydrogenation catalyst and maintaining the concentration of carboxylic acids in the reaction mixture in a 30 predetermined range.

35 21. The process of Claim 20 wherein the precursor is selected from maleic acid or itaconic acid.

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22. The process of Claim 20 or Claim 21
wherein the suitable hydrogenation catalyst comprises
fine metallic particles on an activated porous carbon
5 support comprising by total weight of from about 0.1
to 10 wt % of palladium, about 1 to 20 wt % of rhenium
and optionally from about 0.01 to 1.0 wt % of a metal
component selected from rhodium, cobalt, platinum,
10 ruthenium, iron, thulium, cerium, yttrium, neodymium,
aluminum, praesodymium, holmium, copper, samarium,
europium, hafnium, manganesium, vanadium, chromium,
gold, terbium, lutetium, nickel, scandium and niobium.

23. The process of Claim 19 or Claim 20 or
15 Claim 21 wherein the concentration of acids is 3% to
8% by weight.

24. The process of Claim 19 or Claim 20
wherein the catalyst is of Claim 4 and the support is
20 an activated porous carbon carrier having a surface
area in excess of 1000 m²/g.

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INTERNATIONAL SEARCH REPORT

International Appl. No. PCT/US 91/05165

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)^b

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.C1.5 B 01 J 23/89 B 01 J 23/64 C 07 D 307/08

II. FIELDS SEARCHED

Minimum Documentation Searched⁷

Classification System	Classification Symbols	
Int.C1.5	B 01 J	C 07 D

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched⁸

III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category ^a	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	FR,A,2403824 (ENGELHARD MINERALS & CHEMICALS COMPANY) 20 April 1979 see page 28; claims 1,2,5 ---	1
X	US,A,4795733 (DE THOMAS) 3 January 1989, see column 8; claims 1,2 see column 6; example 1 ---	1,4,5
X	US,A,4302359 (C. MAULDIN) 24 November 1981, see column 10; claims 1,6; column7; example A; column 4, line 42 - column 5, line 14 ---	1,2
Y	---	3,6-22, 24 -/-

* Special categories of cited documents :¹⁰

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step, when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

07-11-1991

Date of Mailing of this International Search Report

5. 12. 91

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

 Danielle van der Haas

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
Y	EP,A,0147219 (DU PONT DE NEMOURS) 3 July 1985, see page 34; claims 1-7; page 10; example 1 (& US,A,4 609 636 cited in the application) ---	3,6-22, 24
A	EP,A,0055512 (THE STANDARD OIL COMPANY) 7 July 1982 ---	
A	US,A,4369129 (C. MAULDIN) 18 January 1983 ---	
A	US,A,4243558 (G. ANTOS) 6 January 1981 -----	

ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.

US 9105165
SA 49884

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 25/11/91. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
FR-A- 2403824	20-04-79	US-A-	4171288	16-10-79
		AU-A-	4009278	27-03-80
		BE-A-	870666	21-03-79
		CA-A-	1116585	19-01-82
		DE-A-	2841417	05-04-79
		GB-A-	1600587	21-10-81
		JP-A-	54056993	08-05-79
		NL-A-	7809430	27-03-79
		SE-A-	7809889	24-03-79
US-A- 4795733	03-01-89	EP-A-	0319116	07-06-89
		JP-A-	1168345	03-07-89
		US-A-	4885410	05-12-89
US-A- 4302359	24-11-81	None		
EP-A- 0147219	03-07-85	US-A-	4550185	29-10-85
		AU-A-	3172789	20-07-89
		AU-A-	3708084	26-06-86
		CA-A-	1268752	08-05-90
		US-A-	4609636	02-09-86
EP-A- 0055512	07-07-82	US-A-	4301077	17-11-81
		CA-A-	1157031	15-11-83
		JP-A-	57109736	08-07-82
US-A- 4369129	18-01-83	None		
US-A- 4243558	06-01-81	None		